TEMPERATURE EFFECT ON POLYMERIZATION KINETICS OF POLYSTYRENE

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ABSTRACT

This research is to study temperature effect on polymerization kinetic of polystyrene. The purposes of this research are to study temperature effect on polymerization kinetics of polystyrene. The experiments for this research were conducted in bulk polymerization of styrene. In this experiment, the temperature will be changing and the value of initiator is constant. Firstly, 3mg of styrene and 2mg of azobisisobutyronitrile solution (in toluene) are placed into the pan. Then, the pan is put into the Differential Scanning Calorimetry at the required temperature. The graph for heat flow versus time is recorded by Differential Scanning Calorimetry software until the reaction is complete. By referring to the graph it can be seen that the reaction rate of polymerization increase with the increase of temperature. As a conclusion, from this research, it can be seen that changing the temperature can affect polymerization kinetic of styrene.

ABSTRACT

Kajian ini adalah untuk mengkaji kesan suhu ke atas kinetik pempolimeran polistirena. Tujuan kajian ini adalah untuk mengkaji kesan suhu ke atas kinetik pempolimeran polistirena. Eksperimen untuk kajian ini telah dijalankan dalam pempolimeran pukal stirena. Dalam eksperimen ini, suhu akan berubah dan nilai pemula adalah tetap. Pertama, 3mg stirena dan 2mg penyelesaian azobisisobutyronitrile (dalam toluene) diletakkan ke dalam bekas. Kemudian, bekas itu dimasukkan ke dalam Kalorimetri Imbasan Pembezaan pada suhu yang dikehendaki. Graf untuk aliran haba berbanding masa yang dicatatkan oleh perisian Kalorimetri Imbasan Pembezaan sehingga tindak balas selesai. Dengan merujuk kepada graf dapat dilihat bahawa kadar tindak balas pempolimeran meningkan dengan peningkatan suhu. Kesimpulannya, melalui kajian ini, ia boleh dilihat bahawa perubahan suhu boleh menjejaskan kinetik pempolimeran stirena.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES

LIST OF ABBREVIATIONS

DSC	Differential Scanning Calorimetry

CHAPTER 1

1.1 Background of Proposed Study

There has been a tremendous increase in polymer production worldwide over the last few decades. Recently, since 2007 there is a steady growth worldwide reflected in increased polymer production and consumption in Asia, where around 30% of the global production is consumed. The number does not include the consumption in Japan which is around 6.5% of world consumption (CIPET, 2012). Because of the increased demand for polymer products (especially plastics), revenue in the global polymer industry in 2011 reached US $454 billion. A compound annual growth is expected to be 3.8% over the next five years (2012-2017), leading to an annual revenue estimation to be around $567 billion. Polymers accounted in this include thermoplastics, thermosets and elastomers. Thermoplastic is a polymer that softens when heated and hardens when cooled. These processes are totally reversible and may be repeated. These polymers consist of linear polymers without any cross-linking in structure where long molecular chains are bonded to each other. Thermosets require heat and pressure to mold them into shape. This polymer cannot be re-melted or reformed into another shape but decompose upon being heated to high temperature. While as, elastomers can undergo large elongation under load at room temperature and return to their original shape when the load is released.(Satish V.,2004) The main reasons for this industry to growth is because of the increasing demand for the plastic materials in end-user markets, technological advances, and strong research and development (R&D) capabilities.(Lucintel,2012) This polymer demand from United States to India will continue to growth around world. (Accenture,2012) Polymer used in a wide range application such as in coating,

adhesives, and structural material.(Davis *et al.*,2004)Polyethylene, poly(vinyl chloride), polystyrene and polypropylene are some examples of plastic in industry.(Gowariker *et al*.,2009)

Polystyrene is playing an important role in this modern life nowadays because of its efficiency, cost-effectiveness and lightweight. The incredible insulating capabilities of polystyrene can maintain the temperature hot or cold. This means that polystyrene meets all the requirement of economical packaging. (Vennyl *et al.,* 2010). Besides that, under production volume, polystyrene is the fourth largest thermoplastic. Polystyrene is used in major market of packaging, consumer/ institutional goods, electrical/ electronic goods, building/ construction, furniture, industrial/ machinery and transportation. (EPA, 2011)

This research is to study temperature effect on polymerization kinetics of polystyrene. Polystyrene can be produced by various methods such as bulk (or mass), solution (a modified bulk), suspension and emulsion polymerizations. (Ding Ru *et al*., 2007) Bulk polymerization (mass polymerization) is a method for the polymerization of monomers and mixtures of monomers. The reaction medium in bulk polymerization is typically solventless because the monomer could be polymerized in the absence of any solvent.(Tartamella *et al.,* 2008)

The global demand for polystyrene and expandable polystyrene increased from 13 million tons in 2000 to around 14.9 million tons in 2010. The demand grew at a Compound Annual Growth Rate (CAGR) of 1.4% during 2000-2010. (Laura, 2012) Polystyrene can be industrially produced by free-radical polymerization using suspension or bulk technique. (Gowariker *et al.,* 2009)

1.2 Problem Statement

This research is about temperature effect on polymerization kinetics of polystyrene. As a general conclusion from Arrhenius equation, an increase in temperature should be

reflected as an increase in rate of polymerization. This research focuses on analysing the effect of temperature on polymerization, and whether or not an increase in temperature should increase the rate of polymerization. The experiment for this research will be conduct in bulk polymerization of styrene. This research will focus on reaching the highest possible conversion at different temperature.

1.3 Objectives

The purposes of this research are:

- to study temperature effect on polymerization kinetics of styrene.

1.4 Research technique

In order to achieve the objective of this study, the outline research scopes for the current research are as follows:

- The equipment that is going to use is differential scanning calorimetry (DSC).
- The temperature range for polymerization kinetic of polystyrene is from 35˚C to 75˚C.
- The initiator use is azobisisobutyronitrile (AIBN)

1.5 Significance of study

- To analyzing temperature effect on polymerization kinetics of polystyrene.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer

Polymer can be defined as a substance that have high molar masses and composed of a large number of repeating units.(Shakhashiri,2012) In Greek, polymer get it names from the word 'poly' meaning many and 'mer' meaning part. Polymer is a combination of small molecules to form a single long or large molecule.(Gowariker *et al*.,2009) In addition, polymer form from the chemical reaction of a large number of molecules called monomer that are joined together to form a chain. Rudin *et al.*(2012) also stated that polymer means "many parts" and designates a large molecule made up of smaller repeating units.

Polymers are both natural occurring and synthetic.(Shakhashiri,2012) Polymers that are isolated from natural materials are called natural polymers.(Gowariker *et al*.,2009) Some of the natural polymer are proteins, starches, cellulose, and latex.(Shakhashiri,2012) On the other hand, polymers that are synthesised from low molecular weight compounds are called synthetic polymers. Some examples of synthetic polymers are polyetylene, nylon and terylene. Plastic is one of the synthetic polymer which is capable of changing its shape on the application of a force and retaining this shape on removal of this force.(Gupta *et al.*,2010) In addition, polymer also can be dividing into organic and inorganic polymer. Organic polymer is a polymer whose backbone chain essentially made of carbon atoms. Different from organic polymer,

inorganic polymer contain no carbon atom in their chain backbone. (Gowariker *et al*.,2009).

Depends on its uses, a polymer can be grouped as plastic, elastomer, fiber or liquid resin. Elastomer is the polymer that is vulcanised into rubbery products which have good strength and elongation. Some examples of elastomer are natural rubber, synthetic rubber and silicone rubber. Polymers such as nylon and terylene are called fiber when these polymers are drawn into long filament-like materials which its length at least 100 times its diameter. Liquid resin is a polymer that has been used as adhesive, potting compound and sealant in a liquid form. This polymer is called plastic when for instance; it is shaped into hard and tough utilities articles by the application of heat and pressure. The examples are polystyrene, polymethyl methacrylate and poly(vinyl chloride). (Gowariker *et al*.,2009).

2.2 Polymerization

Polymer can be classified by the characteristic of the reactions forming which are addition polymer and condensation polymer depends on its type of polymerization reaction involved in their formation.(Robert,2000) Addition polymer forms when molecules are added together to form product. Most of the addition polymer is made from monomers containing a double bond between carbon atoms. Polyolefins is the most commercial addition polymer. Condensation polymer is form when some atoms in the monomer are released into small molecules like water. (Shakhashiri,2012) Some examples of condensation polymers include polyamides (nylon), polyester and phenol-formaldehyde resins. (Robert, 2000)

Throughout the years, because of the original classification of polymer as either condensation or addition polymer cannot give complete differentiation between two classes of polymer, thus, a new classification has been proposed. This classification had been replaced by step-growth polymerization (condensation) and chain-growth polymerization (addition). (Robert,2000) Chain-growth polymerization is characterised

by a self-addition of the monomer molecules, to each other, very rapidly through a chain reaction and there is no by product is formed. Besides that, the product has same elemental composition as the monomer.(Gowariker *et al*.,2009) Nicholson *et al.(*2006) stated that, high molar mass is produced in chain-growth polymerization. In addition, chain-growth polymerization have three steps which are initiation, propagation and termination.(Gowariker *et al*.,2009) Step-growth polymerization undergo stepwise reaction between the functional groups of reactants. (George,2004) monomer concentration also drops rapidly to zero in the early reaction. (Nicholson *et al*.,2006)

Table 2-1: Differential between chain-growth polymerization and step-growth polymerization. (Robert,2000)

Chain-growth Polymerization	**Step-growth Polymerization**
Only growth reaction adds repeating unit one at a time of the chain.	Any two molecular species present can react.
Monomer concentration decreases steadily throughout reaction.	Monomer disappears early in reaction: at degree of polymerization (DP) 10, less than 1% monomer remains.
High polymer is formed at once; polymer molecular weight changes little throughout reaction.	Polymer molecular weight rises steadily throughout reaction.
Reaction mixture contains only monomer, high polymer, and about 10^{-5} part of growing chains.	At any stage all molecular species are present in a calculable distribution.

2.3 Kinetics of Polymerization

Kinetic has a bearing on the speed of a reaction under a given set of condition such as polymer molecular weight, chemical composition and extent of polymer conversion on how condition effected this kinetic polymerization.(Gowariker *et al*.,2009) According to the relative magnitude of initiation rate, polymerization are divide into rapid initiation and slow initiation. Rapid initiation happens when all the

initiation reactions are completed immediately after the polymerization starts. This is because, when the rate of initiation is much larger than rate of propagation, the sum of polymer produced by initiation is independent to the reaction time. On the other hand, slow polymerization happens when initiation reaction occur continuously in polymerization. This is because, when rate of initiation much smaller than rate of propagation, the sum of polymer chains produced by initiation increase with an increase of reaction time. Rapid initiation has been observed in those initiated by ionic catalysts and in post-effect polymerizations initiated by gamma-ray or light radiation. Meanwhile, slow initiation has been observed in those initiated with free radical initiators, gamma-ray or light irradiation and some ionic catalysts. (Tsutomu *et al,*. 1967)

According to the change in the number of moles of the propagating species with an increase in the reaction time, polymerization can be divided into stationary and non-stationary polymerizations. In a non-stationary polymerization with rapid initiation, the number of moles of the propagating species decreases with an increase in the reaction time. In non-stationary polymerizations with slow initiation it have two cases which are the number of moles of the propagating species increase with an increase of reaction time and in the other case, its decreases. (Tsutomu *et al,*. 1967)

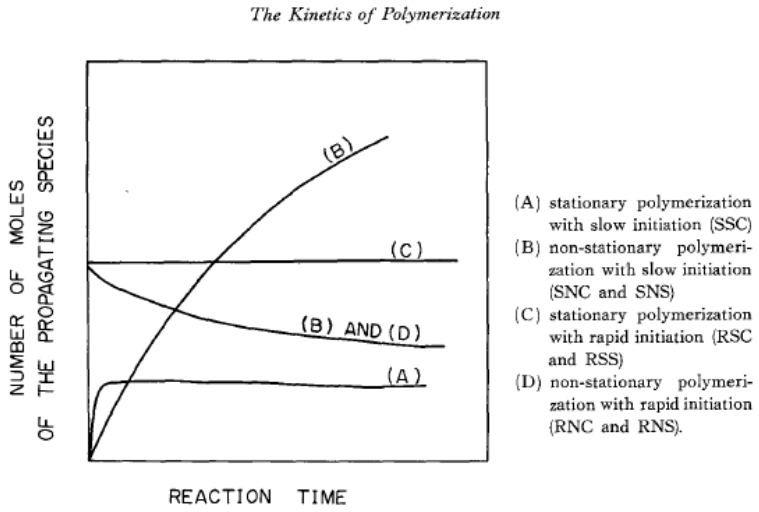
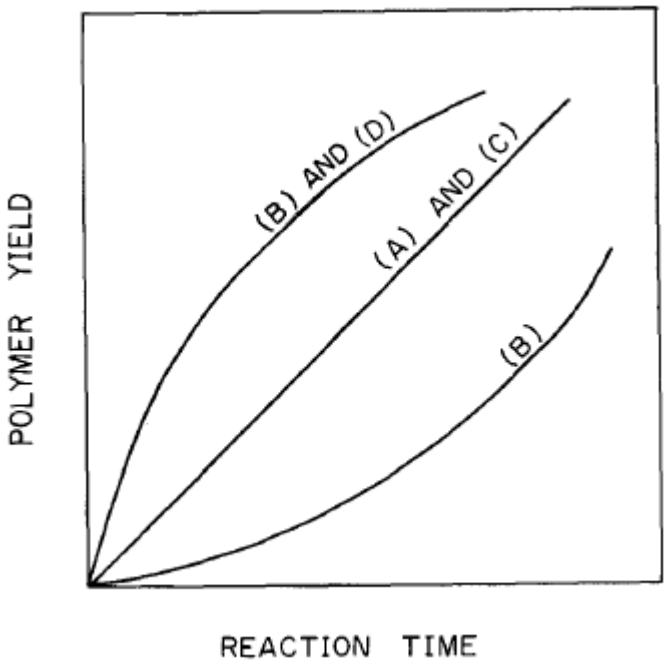


Figure 2-1: Change in the number of moles of propagating species with a change in the reaction time (Tsutomu K *et al.*,1968)



Symbols:
A-D : according to the Figure 2.3.1

Figure 2-2: Dependence of the polymer yield upon the reaction time. (Tsutomu K *et al.*,1968)

2.4 Polymerization of polystyrene

Polystyrene is also known as polyvinyl benzene. Polymerization of polystyrene start in year 1839 but it commercially was realized around 1930. Styrene is produce from ethylene and benzene. Styrene also can be polymerized using radical, coordinator, cationic or anionic. In industrial, polystyrene is produced by free-radical polymerization by suspension or bulk technique. Bulk polymerization is for continuous process while suspension polymerization is for batch process. (Gowariker *et al.*,2009) It is not possible to obtain high polymerization rates due to the nature free radical polymerization and simultaneously get a high molecular weight in bulk or solution process.(Cavin *et al.*,1999)

CHAPTER 3

METHODOLOGY

3.1 Materials

- Styrene
- Aluminium oxide powder
- azobisisobutyronitrile (AIBN) solution is used as initiator

3.2 Equipment

- Differential scanning calorimetry (DSC) Q1000:
  Differential scanning calorimetry is used for studying thermal transitions of solid and liquid. It is especially useful for the thermal characterization of polymers, such as glass transition temperature, crystallization temperature, heat capacity and melting point. (Leuven, 2010)

Figure 3-1: Differential Scanning Calorimetry (DSC) (Leuven, 2010)

3.3 Experiment Procedure

3.3.1 Sample Preparation

Column chromatography method is a method used for preparing styrene without inhibitor. By using this method, the inhibitor in styrene is removed by using aluminium oxide. Firstly, aluminium oxide is put into the column and then the styrene will flow down to the column. After that, the aluminium oxide will absorb the inhibitor in styrene. Finally, the styrene (without the inhibitor) is ready for the polymerization reaction. The purpose of removing the inhibitor is to make sure that the styrene can undergo reaction. This is because, if the inhibitor is not been removed, the inhibitor will prevent the polymerization reaction from occurring.(Lewis,2010). Then, the 3mg sample of the styrene (without inhibitor) and 2mg azobisisobutyronitrile solution is put into the pan using micropipette. To make sure the weight of styrene and azobisisobutyronitrile solution is exactly 5mg, this method is done on the analytical balance.

3.3.2 Experiment to study temperature effect on enthalpy of polymerization kinetic of polystyrene.

Fistly, the pan with the sample solution and initiator is covered with the lid. Then, the weight of this pan with lid and its sample solution is measured by analytical balance to get the sample mass weight. For the reference mass, the weight of the pan with lid without any sample is measured. After that, in order to get sample size, the mass weight is minus with the reference mass. The weights of sample size need to be make sure exactly 5mg because this sample size weight is going to be constant in this experiment. The next step both of the reference lid and sample lid is put into the heater. Then, all the measurement is recorded in the differential scanning calorimetry software. The temperature of the polymerization of polystyrene is set at 35˚C. After that, the differential scanning calorimetry is run. Then, the graph for heat flow versus time is recorded by Differential Scanning Calorimetry software until the reaction complete. The experiment is repeated using different temperature but with constant sample solution and initiator. This experiment is run for 300 minutes (5 hours) for every sample.

3.3.3 Flow diagram of experiment

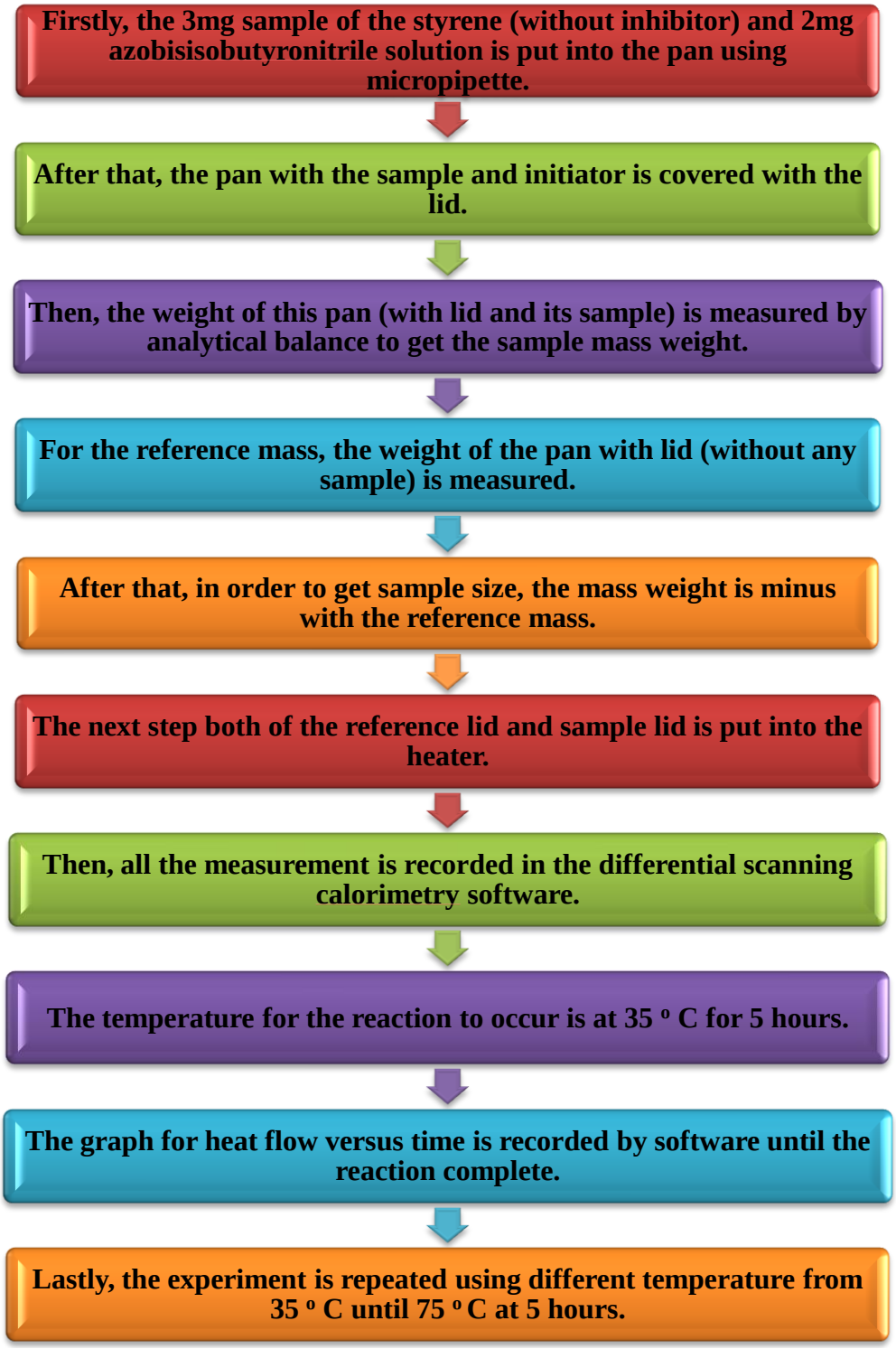


Figure 3-2: Flow diagram of the experiment

FIGURE 3-3: Styrene, azobisisobutyronitrile solution and aluminium oxide powder

Figure 3-4: Equipment for experiment

Figure 3-5: Aluminium Oxide Powder

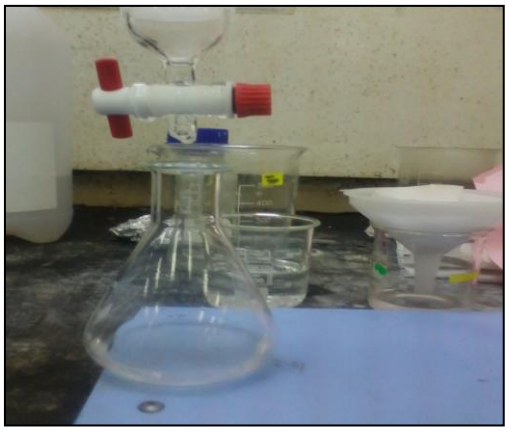


Figure 3-6: Filtration to remove inhibitor from styrene using aluminium oxide

Figure 3-7: Styrene without inhibitor

Figure 3-8: Differential Scanning Calorimetry (DSC)

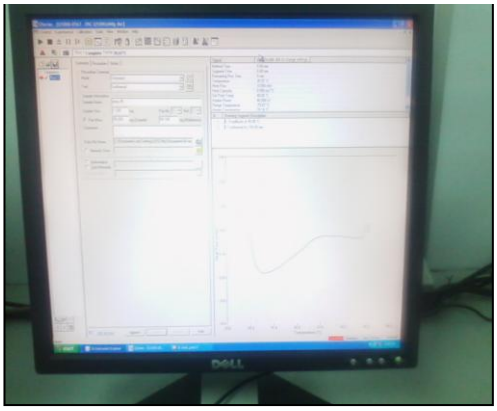


Figure 3-9: Result Analysis from Differential Scanning Calorimetry

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

The purpose of this research is to know the temperature effect on polymerization kinetics of polystyrene. This experiment is to analyse the effect of polymerization of polystyrene with change temperature and constant initiator. The parameter involved is temperature.

4.2 Polymerization of Polystyrene for all temperature

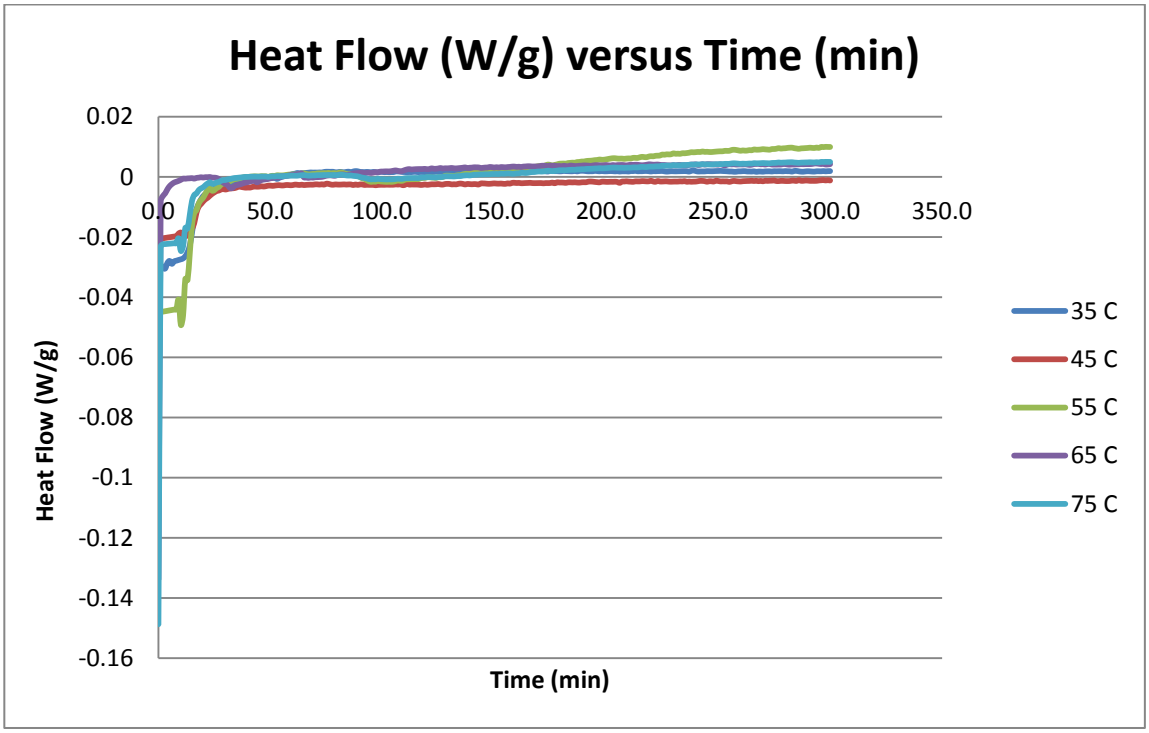


Figure 4-1: Polymerization of Polystyrene for all temperature

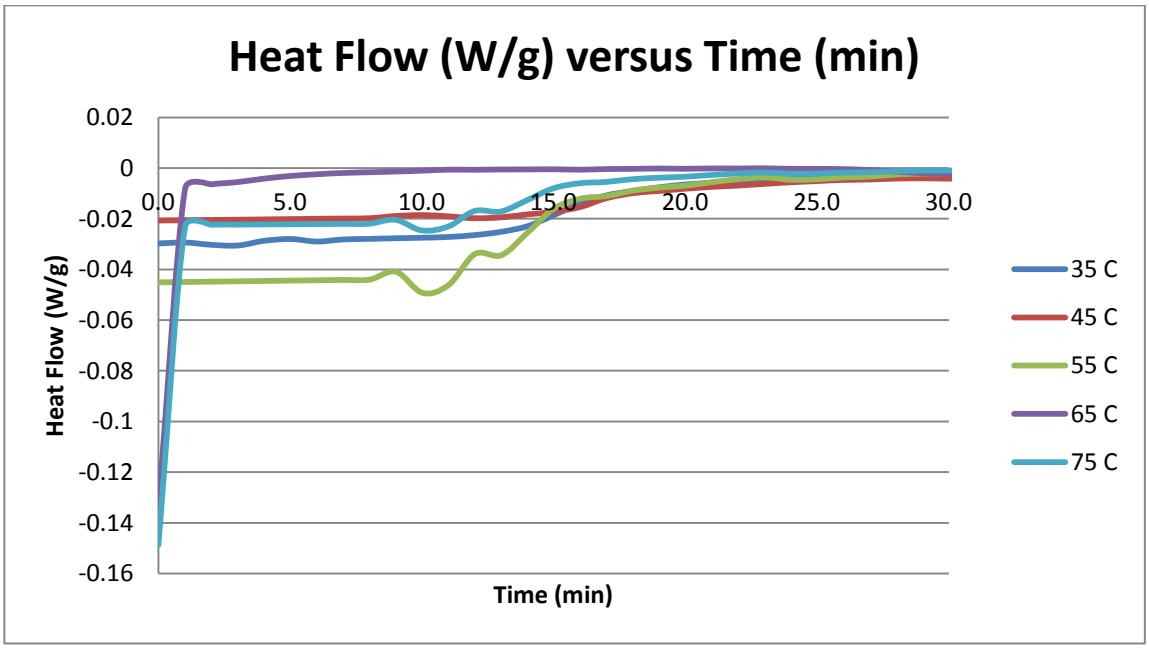


Figure 4-2: Polymerization of Polystyrene at all temperature with time is 30 minutes.

4.2.1 Discussion

Figure 4-1 showed the graph of polymerization of polystyrene at all temperature which are 35˚C, 45˚C, 55˚C, 65˚C and 75˚C until the time 300 minutes. This experiment is done isothermally. Firstly, for the temperature 35˚C, the graph of this temperature that recorded by differential scanning calorimetry can be seen from Appendix B. By referring to the graph of polymerization of polystyrene above, the graph showed that the polymerization reaction of 35˚C starts at the heat flow of -0.029732 W/g. This reaction starts in exorthermic reaction. From the graph, it can be clearly see that the heat flow for polymerization reaction of polystyrene start to constant at 0.001140 W/g at time 63 minutes.

Secondly, at the temperature 45˚C, the reaction of polymerization starts at heat flow of -0.02064982 W/g. The graph of this temperature can be seen at Appendix D. In addition, the polymerization of polystyrene at temperature 45˚C starts to constant at time 163 minutes with heat flow of -0.002082073 W/g. Thirdly, for the temperature at 55˚C, the graph from the differential scanning calorimetry can be seen at Appendix F. In this

graph, polymerization of polystyrene at 55˚C starts at heat flow -0.04511792 W/g. The heat flow only constant at time 41 minutes at 0.00007 W/g until the time 77 minutes with the heat flow at 0.00001 W/g. Then, the graph heat flow continues to fluctuation and the values keep increase until 300 minutes.

Furthermore, at temperature of 65˚C, the reaction of polymerization takes place at the heat flow of -0.1338 W/g. These polymerization reactions of polystyrene become constant at the time 109 minutes at the heat flow of 0.00195 W/g. The graph from differential scanning calorimetry at this temperature can be seen at Appendix H. Lastly, at the temperature 75˚C, the reaction starts at heat flow of -0.1488W/g. The reactions become constant at the 34 minutes with heat flow of -0.00039 W/g. the graph of this temperature that recorded by differential scanning calorimetry can be seen from Appendix J.

By referring to the graph above, Figure 4-1 showed the graph of polymerization of polystyrene at all temperature which are 35˚C, 45˚C, 55˚C, 65˚C and 75˚C until the time 300 minutes while as Figure 4-2 showed the graph of polymerization of polystyrene at all temperature but the data is only for the time until 30 minutes. Basically, these two graphs is the same graph. Only for the graph at Figure 4-2, the data is limited so that, the pattern of the graph can be clearly seen.

The graph at Figure 4-2, showed that the pattern of initial reaction of polymerization of polystyrene. By combining the entire graph with different temperature, it can be see obviously that how the reaction of polymerization starts to react. As the temperature for reaction of polymerization of polystyrene increase, the rate of initial reaction also increases. It has been approved from the graph in Figure 4-2 that temperature at 75˚C has faster initial rate of reaction followed by others temperature.

Besides that, the patterns of polymerization reaction that can be seen from the above graph is, from the time is zero until 15 minutes, the reaction of polymerization of polystyrene is rapidly polymerized. But, as the reactions starts to approach 20 minutes to

30 minutes and above, the reaction starts to become constant. This is because, most of the polymerization reaction is finished at this point. That's why the graph in Figure 4-2 only focused at 30 minutes. In this experiment, all the reaction happens in exorthermic reaction. Therefore, it work on theory that the higher the reaction rate, the higher the polymerization reaction.